

CO PRETREATMENT AND LIQUEFACTION OF SUBBITUMINOUS COAL

S. C. Lim, R. F. Rathbone, E. N. Givens and F. J. Derbyshire,
University of Kentucky Center for Applied Energy Research,
3572 Iron Works Pike, Lexington, KY 40511-8433.

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Abstract

A Wyodak subbituminous coal was pretreated at 300°C at various CO partial pressures in aqueous NaOH. Up to one-third of the oxygen is removed both in the presence and absence of CO. Oxygen-rich, water soluble humic acids are formed in the absence of or at low CO pressures; at 800 psig CO, water soluble product is absent. Higher CO conversions to hydrogen via the water gas shift (WGS) reaction was observed at lower pressures with higher H₂ consumption occurring at the higher pressures. Pyridine solubility and optical microscopy of the pretreated material indicate major reconstruction of the coal structure. Liquefaction of the pretreated material at 400°C in hydrogen/tetralin indicates that pretreated coal reacts faster giving higher conversion and lower hydrogen consumption than raw coal.

INTRODUCTION

Pretreating coal prior to liquefaction has been shown to result in higher yields of product through a net reduction of retrograde reactions. The methodology can vary from treatment of coal through demineralization,^{1,2} acid-washing, solvent swelling,^{3,4} alkylation,⁵⁻⁷ dissolution with strong acids and bases,^{8,9} catalytic reactions,¹⁰ or by the presence of hydrogen.¹¹ Solomon et al.¹² identified at least two distinct cross-linking events when coals are heated; one applies primarily to low-rank coals and occurs at lower temperatures simultaneous with CO₂ and H₂O evolution¹³ that correlates with loss of carboxyl groups and occurs prior to bridge breaking or depolymerization reactions. A second event that is exhibited by higher rank coals occurs at moderate temperatures simultaneous with methane formation subsequent to the initial bridge breaking reactions and correlates best with methane formation. For lignites, these cross-linking reactions begins at about 200°C while the corresponding reaction for higher rank coals begin at temperatures above 400°C.¹²

Aqueous treatment around the supercritical temperature of water, i.e. ~372°C, is also known to cause significant changes in coal which enhance coal conversion under a variety of process conditions.^{14,15} Illinois No. 6 coal, pretreated with steam at 50 atm between 320-360°C, provided a two fold increase in liquid yields and a 20% increase in total volatile yields when pyrolyzed at 740°C.¹⁶ Pretreated coal had lower oxygen content, exhibited reduced hydrogen bonding, had increased pore volume,¹⁷ and had twice as many hydroxyl groups than the starting coal.¹⁸ Steam inhibited retrograde reactions of the phenolic groups that were evolved.^{17,19}

Generally, coal conversion in aqueous systems to which CO and base are added, is higher than in straight aqueous systems or in hydrogen/donor solvent,²⁰ especially for lower rank coals.²¹⁻²⁵ In the CO/H₂O/base system the water-gas shift conversion occurs²⁶ (CO+H₂O→H₂+CO₂) which involves the intermediacy of the formate anion, HCO₂⁻.²⁷ In the study reported here the effect of this reaction system on subbituminous coal at temperatures around 300°C has been investigated. Substantial changes to the coal

substructure have been identified and the liquefaction of the pretreated coal in hydrogen donor solvent has been evaluated.

EXPERIMENTAL

Materials - Reagents were purchased as follows: 99% purity UV grade tetralin, high purity tetrahydrofuran (THF), and high purity pentane were Burdick & Jackson Brand from Baxter S/P; UHP 6000# hydrogen was supplied by Air Products and Chemicals, Inc. A sample of Wyodak Clovis Point coal was supplied by the Wilsonville Advanced Coal Liquefaction Research and Development Facility and had been ground to -200 mesh, riffled and stored in a tightly sealed container. Analysis of the coal is presented in Table 1.

Procedures - Pretreatment experiments were conducted by adding the specified amounts of coal, distilled water, and NaOH to a 25 ml vertical reactor which was sealed and pressurized with CO. The pH of the starting solution was between 13-14. After leak testing, the reactor was submerged in a fluidized sandbath at 300°C and shaken at a rate of 400 cycles per minute. At the end of the reaction period, the reactor was rapidly quenched to room temperature. Gaseous products were vented into a collection vessel and analyzed by gas chromatography. Solid and liquid products were scrapped and washed from the reactor using water and then filtered, and 'freeze dried'. The pH of the aqueous layer was between 5 and 6. Subsequently the sample was dried at 80°C/25 mm Hg for 60 min. In several experiments the insoluble material was placed in a Soxhlet thimble, extracted with THF for 18 hours, and dried overnight at 80°C/25 mm Hg. Ashing of the water and THF insolubles indicated >95% of the Na fed as NaOH reported to the aqueous layer. Soluble material was concentrated by removing excess THF to which was added a 50:1 excess volume of pentane and the mixture placed in an ultrasonic bath for 3 min. The insolubles were removed by filtering and the solubles recovered after evaporating the pentane. The water soluble fraction was acidified with HCl to precipitate humic acids which were centrifuged, collected and dried. The aqueous layer was extracted with ether. Recoveries and products are reported on an maf basis calculated by subtracting the coal ash from the total THF insolubles. Na product is assumed to report completely to the aqueous phase.

Liquefaction experiments were performed by placing raw or pretreated coal and tetralin (2:1 tetralin:coal) in the reactor described above and submerging the reactor in a sandbath at 400°C for periods from 15 to 60 min in 800 psig (cold) H₂. The reactor was rapidly cooled and gaseous products collected. The solid/liquid products were separated into THF insoluble (IOM plus ash), THF soluble/pentane insoluble (PA+A) and pentane soluble (oils) fractions. Conversions and product yields are reported on an maf basis by assuming complete recovery of the ash in the THF insolubles.

Analyses - FTIR transmittance spectra were obtained on a Nicolet Model 20SX spectrometer using KBr pellets of the parent and demineralized coals. Carbon, hydrogen and nitrogen were determined on a Leco Model 600 combustion analyzer. Total sulfur was determined according to ASTM D4239-84 with a Leco Model SC32 combustion-IR analyzer.

Optical Microscopy - Samples of coal, pretreated coal, and liquefaction residues were prepared for microscopical examination by mixing with epoxy resin, placing the mixture into a small cylindrical mold, and allowing the epoxy to harden. A sample surface was then ground and

polished on a polishing wheel using a series of SiC grits and alumina polishing compounds. Microscopical observations were conducted using a Leitz MPV Compact polarizing microscope-photometer. As a qualitative measure of the acidic oxygen functional groups in the feedstock and pretreated coal, a freshly polished surface of the coal-epoxy pellet was immersed in aqueous KOH (pH = 13), rinsed, and then placed in a Safranin-O (a cationic dye) water solution. This procedure has been used as a petrographic method for detecting weathering in coals.^{28,29} This provides a measure of the number of carboxyl and phenolic groups in the coal; the more intense the staining of the polished coal surface, the greater the proportion of acidic oxygen functional groups.

RESULTS AND DISCUSSION

CO Pretreatment of Coal - The yields on an maf basis ranged from 75-92 wt% for water insoluble products and up to 7 wt% for water soluble products as presented in Table 2. All of the unaccounted for organic matter plus water and CO+CO₂ produced from the coal is lumped into Oil+Gas+Water. Total elemental recoveries based upon analysis of the water-insoluble material, or the subdivided PA+A and THF insoluble fractions, and humic acids indicate generally complete carbon recovery, especially at the higher CO pressures. The minor amounts of carbon associated with direct elimination of CO and CO₂ from the coal, which would be less than 1 wt%, plus the ether extract, which was formed only at the lower CO pressures, are not included in these values. Combined hydrogen recoveries ranged from 81% in the absence of CO to greater than 100% at higher CO pressures, and parallel the higher H₂ gas consumptions. Because of the small magnitude of the nitrogen and sulfur contents in the coal these numbers show greater scatter. A rather uniform 40 ± 4 wt% oxygen loss was observed. Based upon ash measurements, Na, added as NaOH, reported exclusively to the water phase.

The highest yield of water soluble product occurs in the complete absence of added CO with its yield steadily decreasing as CO concentration increases. At 800 psig it is completely absent. On the other hand, water insoluble product, as well as the PA+A portion of that product, is higher at higher CO pressures. Significantly, in the absence of CO, the PA+A fraction is completely absent. The yield and H/C atomic ratios of water insoluble product increase simultaneously.

The WGS reaction was approximately 80% complete at the lower CO concentrations versus only 39-53% complete at the higher pressures. Based upon the 4 fold greater CO concentration present at the higher pressure, twice as much H₂ is present at this concentration at which much higher levels of H₂ are consumed. At the lower CO concentrations the observed lower PA+A yields, the higher water insoluble product yields, and the generally higher oil+gas+water yields may be due, in part, to pyrolysis processes which dominate the competing hydrogenation reactions in the more hydrogen deficient environment. Data from the run in the complete absence of CO, where PA+A is absent and the highest yield of water soluble product was obtained, supports this view.

In each of the runs sufficient water is present to maintain a liquid phase at reaction temperature. The results suggest that increasing water concentration gives higher coal conversion at both 200 and 800 psig CO. The WGS reaction appears to show no sensitivity to water concentration in these runs probably because of similar water partial pressures. At this point whether water concentration affects the reaction remains unclear.

Pyridine extraction showed that 60 wt% of pretreated coal prepared at 800 psig CO pressure was soluble versus only 4.5 wt% solubility of the starting coal (Table 3). Pyridine solubility was lower for water insoluble products prepared either at low CO concentrations or in the absence of CO. Pyridine solubility qualitatively reflects the degree of cross-linking in the sample. This value plus the increased H_2 consumption and the absence of any significant reaction in a H_2 environment under these conditions,³⁰ suggest that coal depolymerizes into smaller fragments which are stabilized by the *in-situ* hydrogen generated during the WGS reaction. The poorer result observed at lower CO concentrations suggest rapid depletion of the CO which converts to CO_2 and H_2 before any significant coal upgrading takes place. This is consistent with a reaction path in which the coal structure is stabilized and hydrogenated by the active WGS intermediate.

Optical microscopy showed significant morphological changes in the coal structure of the water insoluble product prepared at the higher CO pressure (Run 45). The structure was completely melted and agglomerated to form large, coherent masses as compared to the original coal (Figure 1). The treated material contained abundant pores ranging from submicron to tens of microns in size, some of which were filled with solid homogeneous bitumen-type material which was fluorescent under ultraviolet illumination, suggesting a high-hydrogen content. The reflectance of the surrounding more abundant altered vitrinite (0.43%) was close to the original coal (0.39%) and showed no visible fluorescence. Staining of the samples with Safranin-O indicates that some of the oxygen functional groups were removed during pretreatment which agrees with the elemental analysis.

FTIR data indicate partial decarboxylation occurred during pretreatment. The intensity of the carbonyl absorption, which appears as a shoulder at 1703 cm^{-1} on the relatively intense aromatic stretching vibration at 1600 cm^{-1} , is reduced in the pretreated coal.

Liquefaction of Pretreated Coal - THF conversions for liquefaction of pretreated coal in hydrogen and tetralin were 60.8 wt.% at 15 min and 83.2 wt.% at 60 min. The corresponding values for raw coal were higher: 49.4 wt.% at 15 min and 74.8 wt.% at 60 min (see Table 4). The increase in THF conversion at 15 min reported mainly to the PA+A fraction while in the 60 min run the improvement in conversion reported to the oil fraction. The $CO+CO_2$ yields for pretreated coal were significantly reduced for both 15 and 60 min runs suggesting significant elimination of carbon oxides during pretreatment.

Both gaseous H_2 and total hydrogen consumption, the latter which includes the sum of gaseous H_2 and hydrogen from tetralin, were determined. Hydrogen consumed in liquefaction of the pretreated coal over the reaction period from 15 to 60 min is nearly constant even though THF conversion increases by 22 wt%. By contrast, raw coal showed a larger increase in total hydrogen consumption over the period.

CONCLUSIONS

Low temperature CO pretreatment of coal promotes formation of a material through hydrogenation and modification of the coal structure which is more reactive than the starting coal. Retrogressive reactions competing for hydrogen during liquefaction apparently have been quenched leading to a more effective utilization of hydrogen.

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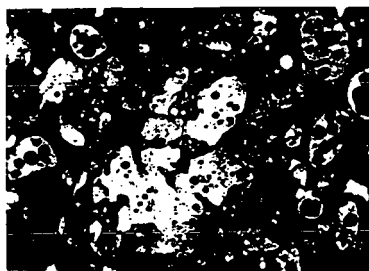


Figure 1. Reflected white-light photomicrographs of Wyodak coal (left) and CO-pretreated coal (right), at 625X. Width of each field of view is approximately 165 microns.

Table 1. Analysis of Wyodak Clovis Point Coal

Composition, wt % maf	
Carbon	71.0
Hydrogen	4.9
Nitrogen	1.3
Sulfur	1.1
Oxygen (by difference)	21.7
Ash, wt% dry coal	6.94
H/C Ratio	0.83

Table 2. Product Distribution from CO Pretreatment of Coal^a

CO, psig cold	200	200	400	800	800	800 ^b
Added water, ml	2	6	4	2	6	6
Products, wt% maf coal						
Water Insoluble	80.8	74.7	90.0	91.7	89.7	80.0
PA+A ^c	2.2	5.5	17.2	17.6	18.0	-
THF Insoluble	78.6	69.2	72.8	74.1	71.7	80.0
Water Soluble						
Humic Acids ^d	5.1	5.5	2.7	-	-	7.0
Ether Extract ^e	1.1	0.5	-	-	-	-
Oil+Gas+Water ^f	13.0	19.3	7.3	8.3	10.3	13.0
Elemental Recovery ^g						
Carbon	93	-	101	101	97	97
Hydrogen	84	-	99	103	107	81
Nitrogen	79	-	120	99	91	115
Sulfur	62	-	60	67	97	51
Oxygen ^h	64	-	66	60	59	56
WGS Conversion ⁱ	78	82	47	39	53	-
H ₂ Gas Consumed ^j	-	8	13	22	26	-
H/C Atomic Ratio ^k	0.75	-	0.83	0.85	0.92	0.71
Run Number	52	48	46	49	45	69

^a 2 g dry coal, 4.4 wt% NaOH on maf coal^b 100% Nitrogen^c THF soluble-pentane insoluble^d Precipitated from acidified aqueous phase^e Ether extract from acidified aqueous phase^f Oil+Gas+Water=100-[water soluble (maf)+water insoluble (maf)]^g Total in combined water soluble + water insoluble^h Oxygen analysis by differenceⁱ WGS = H₂O gas shift; % WGS Conv = $[(CO_{in}-CO_{out})/CO_{in}] \times 100$ ^j H₂ Consumed is [mg H₂(from WGS)-mg H₂(final)]/g maf coal^k Ratio for water insoluble product.

Table 3. Pyridine Extraction

Sample ^a	Pyridine Soluble, wt% maf
Wyodak Coal	4.5
N ₂ /6 ml H ₂ O/NaOH	6.4
200 psi CO/6 ml H ₂ O/NaOH	9.0
800 psi CO/6 ml H ₂ O/NaOH	60.0

a. 1.0 g water insoluble product extracted with 300 ml of pyridine in Soxhlet apparatus for 18 hours.

Table 4. Liquefaction of Raw and CO Pretreated Coal^{a,b}

Coal	Raw	Pretreated	Raw	Pretreated
Time, min	15	15	60	60
THF Conv, wt% maf coal	49.4	60.8	74.8	83.2
Products, wt% maf coal				
PA+A	34.3	47.0	42.8	41.8
Oils+Water	9.9	11.6	26.3	38.9
CO+CO ₂	5.0	2.0	5.4	1.9
HC Gases	0.2	0.2	0.3	0.6
H ₂ Gas Consumed ^c	11	19	17	18
Total H ₂ Consumed ^d				
Run Number	79	81/82	85	86

a. Pretreatment: 800 psig CO cold, 6 ml water, 4.4 wt% NaOH on dry coal, 300°C, 1 hr.

b. Liquefaction conditions: 400°C, 800 psig H₂ cold, 2 g pretreated coal, 2 g tetralin.

c. H₂ Gas Consumed = $[H_{2\text{ in}} - H_{2\text{ out}}]/\text{coal}$ (mg/g maf coal); excludes H₂ consumed by tetralin.

d. Includes both gaseous H₂ and hydrogen consumed from tetralin.